APPARENT DEPOSITION VELOCITY AND COMPENSATION POINT OF AMMONIA INFERRED FROM GRADIENT MEASUREMENTS ABOVE AND THROUGH ALFALFA

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Abstract—Understanding the cycling of ammonia between croplands and the atmosphere is of importance to agriculturalists and atmospheric scientists. Flux densities of gaseous ammonia (NH_3), particulate ammonium (NH_4^+), and total ammoniacal nitrogen (AN) were measured using an aerodynamic method above an alfalfa (*Medicago sativa*, L.) canopy between April and July 1981 at a rural location in central New York State. In air not influenced by local sources, NH_3 and NH_4^+ averaged 1.5 and 3.0 ppb, respectively, at 1 m above the crop. Ambient NH_4^+ varied consistently with synoptic air masses, being lowest (2.3 ppb) for NW and highest (6.4 ppb) for SW flows. Concentrations and gradients of both species were higher during periods of hay harvest. Gradients of NH_3 were much steeper than those of NH_4^+ within the alfalfa canopy, but NH_4^+ contributed appreciably (36% on average) to above-canopy AN gradients. Alfalfa's NH_3 compensation point was estimated by combining concentration and gradient data with transport resistances. Gaseous gradients indicated a compensation point of 2 ppb, lower than previously published estimates. Conversion of NH_3 to NH_4^+ within the canopy air could have reduced NH_3 gradients and caused a low estimate of the compensation point. Acidic aerosols, by keeping NH_3 levels low, may compete with plants for NH_3. Future studies of ammonia exchange should distinguish between NH_3 and NH_4^+ if flux densities are to be related to ambient conditions. Total AN level is a poor predictor of soil–plant–atmosphere ammonia exchange since high AN was frequently associated with low NH_3, and NH_3 is more surface reactive than NH_4^+,

Key word index: Aerodynamic method, ammonia, ammonium, canopy resistance, dry deposition, *Medicago sativa*, micrometeorology.

1. INTRODUCTION

In calculating global ammonia cycling, ambient concentrations of gaseous ammonia (NH_3) and particulate ammonium (NH_4^+) have commonly been combined with assumed deposition velocities to calculate average flux densities. Several such studies have concluded that dry deposition exceeds wet deposition and that total deposition exceeds identifiable sources (Söderlund and Svensson, 1976; Rosswall, 1981; Stedman and Shetter, 1983). Such results have been interpreted as indicating that there must be unidentified sources of atmospheric ammonia, and agricultural crops have been suggested as probable candidates. Dawson (1977) argued that large dry deposition fluxes and major unidentified ammonia sources were unlikely. Possible explanations for excessively large estimates of dry deposition include: (1) concentrations have been overestimated or (2) the equilibrium concentrations of the absorbing surfaces are not negligible.

Average tropospheric NH_3 concentrations were formerly assumed to be in the range 6–10 ppb (Hitchcock and Wechsler, 1972; Almquist, 1974; Holland, 1978; Crutzen, 1983). More recent evidence suggests NH_3 in clean air is usually lower, in the range of 0.01–3.0 ppb (Lau and Charlson, 1977; Brosset, 1980; Hoell et al., 1980; Cadle et al., 1982; Harward et al., 1982; Allen et al., 1988; Harrison et al., 1989). Older trapping methods, which employed inert pre-filters to remove NH_4^+ ahead of NH_3 collection, were subject to errors in that an uncertain fraction of the particulate material probably volatilized off the filter and was captured as 'artifact' NH_3 (Ferm, 1979).

Tropospheric NH_4^+ (solid or liquid phase), expressed as ppb (mole fraction), is often higher than that of NH_3, expressed as the equivalent ppb (volume) (Healy, 1974; National Research Council, 1979; Stedman and Shetter, 1983; Cadle et al., 1985; Mulawa et al., 1986), and is frequently associated with partially-neutralized acid sulfate aerosols and, in some areas, with nitrate (Kadowaki, 1976; Charlson et al., 1978; Brosset, 1980; Lewin et al., 1986; Erisman et al., 1988; Wall et al., 1988). The sulfate aerosols usually have diameters on the order of 0.1 μm (Kadowaki, 1976; Charlson et al., 1978; Brosset, 1980; Cadle et al., 1985) while nitrate aerosols tend to be bimodal (Wall et al., 1988). It is generally thought that sub-micron aerosols

have deposition velocities an order of magnitude lower than reactive gases (Slinn, 1982; Garland and Cox, 1982; Cadle et al., 1985; Mulawa et al., 1986; Nicholson, 1988), though there is not universal agreement on this point (Wesely et al., 1977, 1985; Sievering, 1982; Hicks et al., 1986).

The magnitude of the exchange of fixed N compounds between vegetation and the atmosphere is unclear. Wetselaar and Farquhar (1980) and Hooker et al. (1980) reviewed evidence that the absolute amount of N in the above-ground portion of crop plants often declines between flowering and harvest; declines which could not be accounted for by translocation to roots. Stutte and Weiland (1978) and Weiland and Stutte (1979) showed that several plant species evolved considerable amounts of fixed N, possibly in the form of ammonia, in association with transpiration. Losses of N from plant tops could occur continuously or intermittently (Lemon and Van Houtte, 1980) yet only become evident from total N measurements when the rate of loss exceeds the rate of uptake.

Farquhar et al. (1980) reported that plants have an 'ammonia compensation point', a concentration at which healthy leaves neither gain nor lose NH_3. They reported that the NH_3 compensation points of several species ranged from 3 to 6 ppb and had a strong temperature dependence; however, alfalfa (Medicago sativa, L.) was not studied. Meyer (1973) grew several species, including alfalfa, in pots fertilized with ^{15}N labeled $Ca(NO_3)_2$. He reported that alfalfa raised the ammonia concentration of air exiting a growth chamber to 6 ppb, a value intermediate among the species studied. Recent studies have found an amount of N equal to 3–4% of the total N in the plant at harvest may be lost to the atmosphere as NH_3 during flowering and senescence of wheat (Triticum aestivum) (O'Deen and Porter, 1986; Harper et al., 1987) and have suggested that its NH_3 compensation point may be above 25 ppb and variable with growth stage and fertility conditions (Parton et al., 1988).

The objectives of the current research were to determine: (a) the relative contributions of gaseous and particulate forms to observed gradients of AN above and through an alfalfa canopy; (b) to relate observed differences in the behavior of NH_3 and NH_4^+ to local and synoptic conditions; (c) to evaluate the utility of profile measurements for calculating deposition velocities of NH_3 and NH_4^+, and (d) to estimate the compensation point of field-grown alfalfa for NH_3 during dry daytime conditions.

2. EXPERIMENTAL

2.1. Data collection

Gradients of total (gaseous plus particulate) ammoniacal nitrogen (AN) were measured in the center of a 16 ha alfalfa field in central New York during a period from August 1980 to July 1981 as described elsewhere (Dabney and Bouldin, 1985). Measurements of NH_3 and NH_4^+ concentrations during 63 30-min to 2-h sampling periods (runs) between 15

April and 23 July 1981 are reported herein for the first time. During this interval, alfalfa made the bulk of its spring growth, was cut for haylage in early June, regrew, and was cut again for hay in July. Air samples for NH_3, NH_4^+, and AN analysis were obtained from six to 12 heights above and within the canopy. A temperature difference was measured between points 0.5 m and 1.0 m above the canopy and wind speed was obtained with six cup anemometers located at 24-cm intervals between 0.7 m and 1.9 m above the ground. Soil moisture tension at 30-cm depth, soil temperature, air temperature, wind direction, and rainfall were monitored. Fetches over alfalfa exceeded 150 m from southeast to northwest, and were 130 m to the north and east. A poultry house was located about 200 m to the northeast of the sampling site (for details see Dabney and Bouldin, 1985).

Traps for AN and NH_4^+ collection consisted of cellulose filter papers treated with oxalic acid and housed in 25-mm polypropylene holders as previously described (Dabney and Bouldin, 1985). Used alone, the treated filter papers served as traps for total AN, and thus provided an independent measurement against which to check the sum of NH_3 plus NH_4^+ concentrations. When preceded by an NH_3 trap, the treated filter paper served as an NH_4^+ trap. Traps for NH_3 were constructed using a modification of the coated-tube method of Ferm (1979). Coated-tube traps were 50-cm lengths of 5-mm (o.d.). Pyrex tubing treated internally over a length of 35 cm with 2 ml of a 2.5% (w/v) solution of oxalic acid in methanol, dried in an NH_3-free air stream, and sealed at both ends until use. Coated-tube/filter-paper trap combinations were mounted vertically during exposure and were arranged so that the bottoms of small plastic funnels, attached to the untreated tube ends to prevent rain or condensation from being drawn in during sampling, were at different heights above the ground surface. Vacuum was measured at the manifold during each run and, after exposure, flow through each trap was measured individually at the same vacuum with a single flow meter. This arrangement eliminated the need for the flow-restricting orifices and multiple flow meters employed by Ferm (1979).

Treated filter papers and coated glass tubes were individually extracted with 5 ml of water, and ammoniacal N was determined by a modified Berthelot procedure (Dabney and Bouldin, 1985). Extracts of glass-tube traps caused no analytical interference, but extracts of treated filter papers reduced the sensitivity of the colorimetric assay about 10%. Therefore, standards for NH_4^+ and AN determination were prepared using extracts from unexposed filters. This degree of interference was found to be constant for treated filters stored up to several weeks.

2.2. Data reduction

Wind speed, temperature difference and concentration data were fitted to aerodynamic profile models (Brutsaert, 1982) in order to calculate flux densities and concentrations at reference elevations. The zero-plane displacement, d, was set equal to 0.7 times the measured canopy height for transport of momentum and passive scalars (Thom, 1975). Wind speeds, temperatures, and concentrations measured at heights, z, greater than 2 cm above d, were used in linear regression analysis vs $\ln(z - d)$ using an iterative approach to apply stability corrections to the integral form of the one-dimensional transport equations (Dabney and Bouldin, 1985). Wind speed and temperature data were used in (1) with (2) to calculate the friction velocity, u_*, and momentum roughness length, z_{om}, from the slope and intercept, respectively, of the u_c vs $\ln(z - d)$ regression:

$$\frac{u_*}{k} = \frac{u}{\ln[(z-d)/z_{om}] + \Phi_m} = \frac{u_c}{\ln[(z-d)/z_{om}]} \quad (1)$$

$$L \approx -\left(\frac{u_*}{k}\right)^2 \frac{T \ln(z_r - d)}{g \Delta T_c} \quad (2)$$

where u is the mean wind speed; k is von Karman's constant (0.4); Φ_m is an integral stability factor which depends on L, z and z_{om} (Webb, 1970; Dyer and Hicks, 1970; Benoit, 1977); and $u_c = (u - (u_*/k)\Phi_m)$ is a stability corrected wind speed; L is the Obukov stability parameter; g is the acceleration of gravity; ΔT_c is the difference in stability corrected mean temperature at two heights; and z_r is the logarithmic mean of these two heights. Equation (2) follows from the traditional formulation (Brutsaert, 1982, his equation [4.25]) if the eddy diffusivity for sensible heat is taken equal to that for momentum and if the effect of water vapor on buoyancy is ignored. In some cases of strong atmospheric stability, convergence to a stable u_* value did not occur within 15 iterations. In these cases, values of L were manually changed and u_* calculated until a consistent value was obtained.

The resulting L was used in a similar iterative procedure using NH_3 and NH_4^+ concentrations measured more than 2 cm above d to calculate stability-compensated gradients using (3):

$$\frac{N_*}{k} = \frac{N_N - C_{NS}}{\ln[(z-d)/z_{oN}] + \Phi_N} = \frac{C_{Nc} - C_{NS}}{\ln[(z-d)/z_{oN}]} = \frac{\delta C N_c}{\delta \ln(z-d)} \quad (3)$$

where C_N is the measured concentration, N_*/k is the slope of the logarithmic stability-corrected C_N profile and has the same units as C_N, $C_{Nc} = (C_N - (N_*/k)\Phi_N)$ is a stability-corrected concentration, C_{NS} is the apparent surface concentration obtained by extrapolating the concentration gradient to z_{oN} (estimated method discussed in next section), and Φ_N is an integral stability factor appropriate to AN. Apparent flux densities (N) were calculated from (4):

$$N = -Cu_*N_* \quad (4)$$

where C is a unit conversion factor that depends weakly on temperature and the convention that positive flux is a loss from the surface has been adopted.

These procedures allowed simple linear regression to provide estimates and confidence intervals for mean concentrations, profile slopes, and flux densities which were not biased by profile curvature induced by atmospheric stability conditions. Ambient concentrations at a reference elevation of 1 m above d were estimated by applying stability adjustments in reverse to values interpolated from stability-corrected regression lines.

2.3. Resistance formulations

Deposition velocity (v_d) is usually defined as the ratio of the surface flux density of a species (or the negative of a flux density defined as positive upward) to its concentration at a reference elevation. This definition assumes a negligible surface concentration; the difference between ambient and surface concentrations is appropriate if this assumption is not valid. The inverse of a deposition velocity is a resistance to transport.

The total resistance to tranport of mass to plant canopies has been conceptualized as the sum of three components,

$$r_T = r_a + r_b + r_c \quad (5)$$

where r_a is the aerodynamic resistance, r_b is an excess or boundary-layer resistance which arises because the resistance to transport of passive scalars is greater than that of momentum (e.g. $z_{oN} < z_{om}$), and r_c is a canopy resistance which includes stomatal and other resistances (Fowler and Unsworth, 1979; Hosker and Lindberg, 1982; Brutsaert, 1982; Bache, 1986). Some authors have used the term 'surface resistance' for r_c (Garland, 1977; Galbally and Roy, 1980; Colbeck and Harrison, 1985), while others have referred to the sum $r_b + r_c$ as the 'canopy resistance' (van Bavel, 1967; Monteith, 1981).

The aerodynamic resistance, r_a, the ratio of the concentration difference to the flux of momentum, is calculated:

$$r_a = u/u_*^2. \quad (6)$$

The boundary-layer resistance for heat and water vapor over rough permeable surfaces may be estimated:

$$r_b = (Bu_*)^{-1} \quad (7)$$

where B^{-1}, a dimensionless constant whose value for heat and water vapor lies between 2.5 and 7.5 over a wide range of the flow conditions (Garratt and Hicks, 1973; Brutsaert, 1979). Since the molecular diffusivity (D) of NH_3 is similar to that of water vapor ($D = 0.22$, 0.252 and 0.247 $cm^2 s^{-1}$ for heat, water vapor and NH_3, respectively) a similar value of B^{-1} is assumed to also be appropriate. Herein, B^{-1} was taken equal to 5, corresponding to z_{om}/z_{oN} equal to 7.4.

Canopy resistance is often the dominant factor controlling processes where reactive sites are located within plant stomates. Since this is the case both for water vapor and NH_3, and since metabolic resistances to ammonia uptake are likely to be small (Farquhar et al., 1980), the values of r_c appropriate to water and NH_3 transport are likely to be similar. For most arable crops, typical minimum values of r_c are in the range of 50–100 $s m^{-1}$ for water vapor (Monteith, 1981). Non-stressed alfalfa has an unusually low stomatal resistance. Lee and Gates (1964) estimated that the stomatal resistance of alfalfa is 79 $s m^{-1}$; suggesting that an alfalfa canopy with leaf area index of 3–5 may have an r_c value of 20–30 $s m^{-1}$. Measurements by van Bavel (1967) are consistent with this. He reported daytime values of the sum $(r_b + r_c)$ for 45-cm alfalfa were less than 20–50 $s m^{-1}$ for 20 days after irrigation, and then increased with drought stress to 1400 $s m^{-1}$ 10 days later.

In analyzing the present data, estimates of r_a were calculated from (6) for a reference elevation 1 m above d in order to maintain a constant effective elevation despite changing canopy heights. This resistance was combined with r_b from (7) and with ambient NH_3 and NH_4^+ concentrations and gradients to deduce apparent leaf surface values, NH_{3S} and NH_{4S}^+. Finally, assumed canopy resistance values of 25 and 50 $s m^{-1}$ were added to r_a and r_b and were used with ambient NH_3 concentrations and gradients of either NH_3 or AN measured during dry daytime periods to estimate the NH_3 compensation point of field-grown alfalfa.

RESULTS AND DISCUSSION

Summary data of 63 runs when separate NH_3 and NH_4^+ measurements were obtained are reported in Table 1. In this table and subsequent text, ammonia gradients are discussed in terms of the parameter N_* defined as in (3). Reported AN concentrations are based on combined AN and NH_3 and NH_4^+ observations. For runs without N_* estimates, NH_3 and NH_4^+ values reflect only a single observation. For runs with N_* estimates, concentration estimates without confidence intervals were obtained by interpolation using two measurements.

Changes in canopy height (Table 1) reflect the growth and cutting of the alfalfa. Changes in soil suction reflect the occurrence of significant rainfall on 15 May, 13 June and 20 July followed in each case by drying periods. A 'wet' canopy refers to foliage wetted by light or heavy rainfall, while 'dew' refers to the presence of wet foliage attributable to condensation of guttation.

Wind direction, time of day, and level of atmospheric stability were not independent (Dabney and Bouldin, 1985), Prevailing fairweather daytime winds at the study site were from the west. Northwest winds characteristically followed the passage of cold fronts,

Table 1. Soil moisture, canopy condition, gradient, concentration, and flux data from runs in which separate gas and particulate measurements were made near King Ferry, NY

Date	Local time	Soil suct. (kPa)	Surface cond.	Height (m)	Wind dir. (deg)	Temp (°C)	L (m)	u_* (m s⁻¹)	z_{om} (m)	r_a (s m⁻¹)	r_b	N_* AN	N_* NH₃	N_* NH₄⁺	Conc. AN (ppb)	Conc. NH₃	Conc. NH₄⁺	AN flux (g ha⁻¹ h⁻¹)
30.04.81	0829–1022	—	Dew	0.19	295	12	−37	0.18	0.015	57	28	−0.16	−0.37	0.02	3.2±0.5	0.2±5.4	3.0±0.1	0.62
13.05.81	1222–1315	57	Wet	0.34	315	16	−153	0.44	0.033	19	11	0.03	−0.10	0.14	2.0±0.4	1.1±0.5	1.3±3.0	−0.28
13.05.81	2056–2137	58	Dew	0.34	315	9	14	0.16	0.044	55	32	−0.07	0.02	−0.01	2.2±0.2	0.4±0.7	1.9±0.3	0.22
14.05.81	0926–1028	>58	Dry	0.34	295	17	−7	0.21	0.032	36	24	−0.02	−0.06	−0.01	1.9±0.3	0.3±0.6	1.5±0.2	0.08
17.05.81	1355–1511	4	Dry	0.36	335	12	−41	0.40	0.041	19	12	−0.12	0.01	−0.28	2.3±0.5	0.7±0.4	1.3±3.5	1.08
18.05.81	1311–1530	10	Dry	0.40	315	14	−44	0.49	0.037	17	10	−0.11	0.04	−0.03	1.5±0.2	1.0±4.0	1.0±0.9	1.15
19.05.81	0956–1049	18	Dry	0.40	315	14	−7	0.17	0.030	45	29	−0.17	0.04	−0.09	2.2±0.2	0.7	1.8	0.64
20.05.81	1453–1547	30	Dry	0.40	315	22	−39	0.30	0.042	26	17	−0.02	0.03	0.10	1.9±0.6	0.9	0.9	0.12
21.05.81	1515–1639	45	Dry	0.40	295	26	−49	0.40	0.048	19	12	−0.20	−0.27	−0.16	3.5±0.3	0.6	2.3	1.70
22.05.81	1328–1438	60	Dry	0.40	315	24	−857	0.49	0.047	16	10	−0.15	0.13	0.31	5.5±2.0	1.3	4.5	1.51‡
22.05.81	2213–2330	60	Dew	0.40	45	10	19	0.21	0.118	28	24	4.08			20.6±3.9	9.2	4.4	−18.52‡
23.05.81	0640–0740	>60	Dew	0.40	70	8	8	0.12	0.040	80	42	0.67	0.76	0.50	13.2±1.8	10.0	7.6	−1.72‡
25.05.81	0947–1108	>60	Dry	0.45	160	28	−128	0.34	0.050	22	15	−0.08			6.6±0.6	0.2	5.8	0.60
01.06.81	1008–1121	>60	Dry	0.65	315	14	−29	0.29	0.062	23	17	−0.17	0.36	−0.28	4.0±0.9	2.7	1.9	1.06
04.06.81	0735–0900	—	Wet	0.70	200	28	−69	0.23	0.047	32	21	0.15	0.02	0.36	8.6±0.6	1.5±1.5	7.8±7.8	−0.72
04.06.81	1501–1557	—	Dry	0.70	290	23	211	0.39	0.042	21	13	−1.22	−0.35	−0.22	6.3±0.9	4.3±0.2	3.4±3.3	9.86‡
05.06.81	1533–1648	—	Dry	0.75	var	29	−11	0.20	0.049	35	26	−0.69			5.5±0.8	2.7	5.1	2.96
09.06.81	1049–1159	—	Wet	0.14	340	23	−34	0.34	0.010	33	15	−0.68	−0.38	−0.30	4.3±1.1	4.0±0.7	1.7±5.4	4.82
11.06.81	1747–1839	—	Dry	0.08	340	23	−144	0.29	0.010	34	17	−0.06	0.06	0.07	7.1±0.5	2.8	4.3	0.38
11.06.81	2141–2302	—	Dry	0.08	var	16	13	0.07	0.022	142	68	−0.15	−0.10	−0.02	7.1±0.4	2.6±0.9	4.6±0.4	0.23
13.06.81	1013–1127	—	Wet	0.08	225	23	−4	0.16	0.008	67	31	−1.64	−0.76	−0.93	13.5±1.0	1.4±1.5	11.7±0.9	5.46
14.06.81	1238–1335	—	Wet	0.08	135	24	−29	0.39	0.012	28	13	−0.22	−0.23	0.07	8.9±0.6	1.4±0.4	7.9±0.9	1.77
15.06.81	1348–1439	1	Wet	0.10	270	33	−14	0.24	0.008	49	21	−3.16	−5.26	−1.81	15.1±4.4	6.4	10.5	15.17‡
15.06.81	2042–2118	1	Dew	0.10	90	23	32	0.17	0.009	71	29	−1.08	−0.59	−0.06	10.6±1.1	5.6±3.1	6.6±6.1	3.87
17.06.81	1456–1603	2	Dry	0.15	270	22	−32	0.29	0.007	41	17	−0.17	−0.11	−0.12	6.5±0.6	2.4±0.4	3.9±0.9	1.07
17.06.81	1936–2036	2	Dry	0.15	360	19	−273	0.18	0.025	52	28	0.17	0.18	−0.04	5.5±0.3	3.4	1.9	−0.63
18.06.81	0453–0538	2	Dew	0.15	110	12	28	0.16	0.019	65	31	−0.17			4.2±0.6	1.9	2.4	0.57
18.06.81	0651–0746	2	Dew	0.15	135	16	−10	0.16	0.011	65	30	−0.30	0.24	0.39	5.9±1.0	3.2	2.9	1.04
18.06.81	1057–1155	4	Dry	0.15	180	24	−7	0.23	0.010	45	21	−0.41	−0.47	−0.21	4.7±0.5	1.5±0.2	2.8±1.2	1.98
18.06.81	1552–1645	4	Dry	0.15	160	27	−32	0.33	0.012	33	15	−0.04			5.2±0.3	2.3	2.8	0.24
27.06.81	1105–1207	20	Dry	0.35	340	23	−26	0.25	0.024	36	20	−0.03	0.08	0.09	4.2±0.5	2.5±3.3	2.6±3.9	0.14
27.06.81	2142–2236	28	Dew	0.35	65	24	9	0.16	0.037	59	31	0.24	0.18	0.03	5.1±0.3	3.1	1.9	−0.82
28.06.81	0819–0924	31	Dew	0.35	180	28	−4	0.13	0.027	62	40	0.03	0.10	−0.09	4.3±1.1	2.7±2.6	1.7±1.2	−0.08
28.06.81	1143–1242	35	Dry	0.35	180	27	−37	0.21	0.024	44	24	−0.03	0.01	−0.11	2.2±0.7	2.1±2.6	0.9±1.6	0.12
28.06.81	1845–2010	42	Dry	0.35	135	22	7	0.15	0.026	74	34	−0.03	−0.07	−0.08	1.9±0.3	0.9	0.9	0.09
29.06.81	1211–1336	54	Dry	0.35	150	27	−41	0.31	0.024	29	16	−0.14	−0.04	−0.05	3.8±0.4	1.5±0.6	2.8±0.4	0.87
29.06.81	1532–1637	60	Dry	0.35	180	29	−72	0.28	0.027	32	18	−0.10	0.08	−0.18	4.2±0.5	1.1±0.5	3.6±2.8	0.58
04.07.81	0800–0855	>60	Dew	0.45	135	29	−211	0.24	0.027	37	21	−0.18	−0.07	−0.12	5.9±0.6	0.4±0.5	5.5±1.0	0.93
05.07.81	1529–1611	>60	Wet	0.45	270	24	−14	0.16	0.033	49	31	−0.21	0.10	0.19	8.3±0.9	0.9±1.1	8.4±4.8	0.70
05.07.81	1937–2043	>60	Wet	0.45	20	29	203	0.13	0.096	44	37	0.06	0.06	−0.01	8.3±1.3	0.7±0.4	7.6±1.0	−0.15
06.07.81	0710–0800	>60	Dew	0.45	90	14	−9	0.12	0.068	52	43	0.07	0.15	−0.08	4.8±0.7	1.4±0.5	3.3±0.3	−0.18
07.07.81	1008–1058	>60	Dry	0.55	315	27	−140	0.35	0.031	25	14	0.14	0.19	0.22	9.2±0.8	2.7±1.8	7.4±2.2	−1.02
07.07.81	1608–1723	>60	Dry	0.55	315	31	−27	0.26	0.035	31	19	−0.04	0.04	−0.04	4.1±0.3	1.7±1.8	2.7±0.4	0.19
07.07.81	2149–2251	>60	Dry	0.55	45	23	3	0.09	0.033	142	58	0.26	0.45	−0.08	13.0±5.1	7.1±1.1	8.2±1.3	−0.46‡

Date	Time	Wind	Surface	z₀	Dir		Comp. pt.											
08.07.81	1411–1502	>60	Dry	0.55	270	32	402	0.47	0.032	18	11	−0.09	0.01	−0.06	10.4±1.0	1.5±9.2	8.9±8.1	0.91
09.07.81	1117–1218	>60	Dry	0.57	295	29	−709	0.41	0.033	21	12	−0.21	−0.02	−0.09	6.5±0.9	1.4±0.7	5.6±2.2	1.70
10.07.81	1232–1335	>60	Dry	0.58	315	28	−71	0.30	0.032	28	16	−0.09	−0.07	−0.01	3.5±0.2	1.8±0.4	1.6±0.2	0.55
10.07.81	2232–2321	>60	Dew	0.58	70	17	3	0.13	0.071	81	38	0.08	0.09	0.03	3.4±0.8	2.2±1.0	2.0±0.5	−0.24
11.07.81	0815–0844	>60	Dew	0.58	125	23	12	0.08	0.015	140	61	−0.02			3.3±0.4	1.0	2.3	0.04
12.07.81	1741–1831	>60	Dry	0.60	295	30	8	0.12	0.018	89	40	−0.21	−0.19	−0.26	2.8±0.8	0.3±0.5	0.9±1.2	0.54
13.07.81	1535–1635	>60	Dry	0.60	270	32	(−100	0.2	0.068§	35	25	0.06	0.07	−0.01	7.6±0.2	1.4±1.1	6.2±1.1	—
14.7.81	0907–0957	>60	Dry	0.60	335	21	−306	0.50	0.032	17	10	−0.05	−0.03	−0.02	1.6±0.6	0.8±0.4	0.8±0.5	0.53
14.07.81	1523–1624	>60	Dry	0.60	315	19	2700	0.47	0.032	19	11	0.14	0.07	0.08	1.2±1.0	1.0±1.0	0.8±0.3	−1.37
18.07.81	1332–1420	>60	Dry	0.62	270	31	17	0.22	0.016	50	22	−0.18	−0.12	−0.23	3.7±0.4	0.6±1.9	2.8±2.8	0.80
19.07.81	1535–1650	>60	Wet	0.65	245	28	4	0.10	0.009	155	52	−0.04	−0.06	−0.01	2.0±0.2	−0.1±0.8	1.9±0.7	0.06
21.07.81	1203–1306	>60	Wet	0.65	270	26	−149	0.15	0.019	65	33	−0.65	−0.17	−0.26	7.3±2.1	0.8±0.0	6.6±3.9	2.06
22.07.81	1720–1827	5	Dry	0.10	335	23	−33	0.31	0.014	34	16	−0.42	−0.29	−0.13	1.8±0.3	1.4±0.8	0.5±0.7	2.65
23.07.81	0725–0744	5	Dew	0.20	115	16	11	0.13	0.027	78	39	−3.50	−4.17	−0.70	17.1±5.4	9.4	5.5	9.63‡
23.07.81	0820–0859	5	Dew	0.10	335	18	−4	0.16	0.012	63	32	−1.47	−1.25	−0.37	3.8±1.2	2.5±0.6	2.0±5.3	4.87
23.07.81	0959–1051	5	Dry	0.10	335	21	−11	0.25	0.015	40	20	−1.45	−1.28	−0.26	3.7±0.6	1.5±5.3	1.9±4.2	7.49
23.07.81	1220–1437	8	Dry	0.10	335	23	−12	0.33	0.014	31	15	−0.60	−0.53	−0.11	3.0±0.2	1.3±2.3	1.6±0.2	4.03
23.07.81	1713–1757	8	Dry	0.10	335	23	−54	0.26	0.008	45	19	−0.28	−0.24	−0.01	2.1±0.2	1.3	1.0	1.52
23.07.81	2130–2208	10	Dew	0.10	45	12	31	0.17	0.026	55	29	−1.26	−1.11	−0.03	5.8±0.7	4.0	3.1	4.73

†Concentration and 95% confidence interval at a height of 1 m above the displacement plane.
§Wind speed data not recorded, indicated values used for stability correction, flux estimates not made.
‡Value represents a correction to data reported in Dabney and Bouldin (1985).

which brought clear cool air from Canada. South and SW flows were characteristic of hot, humid days when visibility was reduced by haze in otherwise clear skies. At night, easterly winds usually resulted from stable drainage flows into the Cayuga Lake valley.

3.1. Gaseous and particulate concentrations

The sum of measured NH_3 and NH_4^+ concentrations was found to agree well with direct measurements of AN concentration made with filter paper traps not preceded by coated-tube traps (data not shown). Tests with traps in series indicated both coated-tube and filter-paper traps recovered NH_3 volatilized into a laboratory air stream with greater than 95% efficiency.

Dabney and Bouldin (1985) previously reported that AN concentrations at a reference height of 1 m were higher during NE and SW flows. The data reported here demonstrate that the makeup of these elevated values differed considerably. Both NH_3 and NH_4^+ concentrations were elevated during NE flows because of local sources (see below); whereas only NH_4^+ concentrations were elevated during SW flows (Table 2). For all flow directions except NE, NH_3 levels averaged 1.7 ppb; whereas NH_4^+ concentrations averaged 2.3 ppb for NW and SE flows and 6.4 ppb for SW flows. High NH_4^+ concentrations during SW flows were frequently associated with very low NH_3 levels (Table 1). Similar observations were made in Ontario by Anlauf et al. (1985) and in Pennsylvania by Lewin et al. (1986) who reported high levels of NH_4^+ were frequently associated with NH_3 levels below 1 ppb.

Both NH_3 and NH_4^+ concentrations at 1-m height were higher during periods within 10 days after hay cutting than during periods preceding cutting (Table 2). During these periods, exposed soil, plant debris,

and hay spoiled by rain made the field itself behave as a local NH_3 source (Dabney and Bouldin, 1985).

Exhaust from one specific pullet house located to the NE of the field contained approximately 900 ppb AN. This exhaust elevated ambient nighttime values before the house was emptied on 1 June and after a new batch of 30,000 chicks was placed in the house on 10 July. Even when this facility was not in use, night-time NH_3 concentrations were frequently elevated, perhaps due to other sources in this mixed-farming area. Similar observations were reported by Tsunogai and Ikeuchi (1968) and Asman et al. (1989). A specific source was noted on the evening of 22 May when the smell of a smoldering bale of alfalfa hay, discarded and ignited at the NE corner of the field (about 150 m from the measurement mast), dominated that of the poultry house. Air samples that intermittently encountered the meandering smoke plume indicated AN concentrations exceeding 3000 ppb existed close to this source. These observations support the speculation of Söderlund and Svensson (1976) that low temperature brush fires may be an important source of atmospheric AN. Controlled burning of agricultural and forest lands is common in many areas should be considered in global and regional AN budgeting.

3.2. Deposition velocities

A deposition velocity, v_{dr}, calculated from meteorological data as the inverse of the sum of r_a and r_b (Table 3), resulted in values similar to the 0.01 m s^{-1} commonly cited as typical for gases depositing on reactive surfaces (Hill, 1971; Hill and Chamberlain, 1976; Walcek et al., 1986). This deposition velocity varied with wind direction in ways which were also associated with differences in atmospheric stability. Depos-

Table 2. NH_3 and NH_4^+ concentrations* at reference elevation of 1 m above d and at leaf surfaces calculated from gradients of gas and particulate species, as influenced by hay cutting period and wind direction

Wind direction	Number of observations	NH₃ Reference NH_3	NH₃ Surface NH_{3s}	NH₄⁺ Reference NH_4^+	NH₄⁺ Surface NH_{4s}^+
		ppb			
Not within 10 days after hay cutting					
NE	6	4.1 ± 1.5	0.1 ± 0.4	5.1 ± 1.2	3.6 ± 2.4
NW	22	1.4 ± 0.2	1.7 ± 0.5	2.3 ± 0.4	2.7 ± 0.3
SE	7	1.6 ± 0.4	2.2 ± 1.2	2.9 ± 0.6	3.5 ± 2.6
SW	5	1.4 ± 0.3	1.6 ± 0.8	6.4 ± 1.3	6.3 ± 0.7
Total	41				
Mean		1.9 ± 0.3	1.5 ± 0.4	3.3 ± 0.4	3.4 ± 0.4
Within 10 days after hay cutting					
NE	2	4.8 ± 0.8	17.9 ± 2.2	4.9 ± 1.7	5.6 ± 2.1
NW	7	2.1 ± 0.4	10.6 ± 2.8	1.8 ± 0.4	4.3 ± 0.9
SE	2	5.4 ± 4.0	38.9 ± 33.8	6.7 ± 1.2	11.5 ± 4.7
SW	4	2.1 ± 1.5	27.8 ± 22.1	7.7 ± 2.2	19.9 ± 8.5
Total	15				
Mean		2.9 ± 0.7	20.0 ± 6.9	4.4 ± 0.9	9.6 ± 2.8

* Mean ± standard error of mean for runs during which NH_3 and NH_4^+ were measured at two or more above-canopy elevations.

Table 3. Aerodynamic resistance (r_a), boundary-layer resistance (r_b), and deposition velocities calculated from the inverse of the resistance sum (v_{dr}) or from gradients, all referenced to 1 m above d, as influenced by hay cutting period and wind direction

Wind direction	Number of observations	Transport resistances*		Deposition velocity			
		r_a	r_b	v_{dr}	NH_3	NH_4^+	AN
		-------- s m^{-1} ------		----------------- m s^{-1} -----------------			
Not within 10 days after hay cutting							
NE	6	76 ± 14	41 ± 4	0.009	0.008	0.001	0.004
NW	22	32 ± 4	19 ± 2	0.024	−0.023	−0.005	−0.010
SE	7	49 ± 7	26 ± 3	0.015	−0.013	−0.006	−0.008
SW	5	38 ± 6	20 ± 3	0.019	−0.007	−0.003	−0.005
Total	41						
Mean		43 ± 4	24 ± 2	0.020	−0.015	−0.004	−0.007
Within 10 days after hay cutting							
NE	2	63 ± 8	29 ± 1	0.011	−0.033	−0.002	−0.028
NW	7	40 ± 4	19 ± 2	0.018	−0.081	−0.033	−0.055
SE	2	53 ± 25	26 ± 13	0.016	−0.060	−0.007	−0.018
SW	4	83 ± 24	34 ± 7	0.010	−0.066	−0.015	−0.021
Total	15						
Mean		57 ± 8	25 ± 3	0.015	−0.068	−0.020	−0.037

* Mean ± standard error of mean.

ition velocity was maximized during near-neutral flows when mixing was dominated by wind shear. The percentages of runs with $L>0$ (when temperature inversions suppressed mixing) were 89, 14, 31, and 30% for NE, NW, SE, and SW flows, respectively.

Apparent deposition velocities, v_d, were determined from gradient data by dividing fluxes calculated from NH_{3*} and NH_{4*}^+ using (4) by ambient concentrations. These values took on both positive and negative values since both positive and negative gradients occurred (Table 1). However, mean values of v_d were consistently negative for both species (Table 3). This result suggests the assumption of zero surface equilibrium concentrations is frequently incorrect and seems to imply surface sources of both NH_3 and NH_4^+. However, as discussed later, the possibility exists that the surface AN source was predominantly NH_3, with NH_4^+ gradients resulting from gas-to-particle conversion.

Gradients of NH_3 were steeper than those of NH_4^+ under both daytime and night-time conditions. During 36 runs when three or more points were available to estimate NH_{3*} and NH_{4*}^+, and where AN_* was simultaneously measured independently (using filter paper traps without preceding coated-tube traps arrayed at several heights), NH_{3*} contributed 63% and NH_{4*}^+ 36% of above-canopy AN_*. Reflecting this, absolute deposition velocity values of NH_3 were larger than those of NH_4^+ (Table 3). These findings are consistent with the hypothesis that NH_3 is the more reactive species, but the magnitude of the difference is less than expected from theory (Nicholson, 1988).

3.3. Surface concentrations

Apparent surface concentrations NH_{3S} and NH_{4S}^+, were higher and more variable during periods within

10 days following alfalfa cutting than during other periods (Table 2). During non-hay cutting periods, NH_{3S} was lower for NE flows than for all other flow direction $(P<0.09)$. Northeast flows occurred almost exclusively at night, and this difference may reflect the low equilibrium value of NH_3 dissolving in dew or guttation; although this interpretation must be considered tenuous because of the possibility of horizontal gradients during NE flows.

The boundary-layer resistance appropriate to submicro aerosols is unknown (Friedlander, 1977; Wesely et al., 1985; Nicholson, 1988). In the present case, even when calculations of NH_{4S}^+ were made as if NH_4^+ had a similar r_b as NH_3, NH_{4S}^+ concentrations tended to follow NH_4^+ concentrations at the reference elevation (Table 2). Only during runs with southerly air flows within 10 days of hay cutting (when AN fluxes and particulate concentrations were both high) did NH_{4S}^+ and NH_4^+ at 1-m elevation differ significantly. Employing a smaller (more probably correct) diffusivity estimate for NH_4^+ would result in larger estimates of r_b and smaller v_{dr}, and would uncouple NH_{4S}^+ and NH_4^+. For this reason, NH_{4S}^+ values in Table 2 are not considered to reflect true surface conditions.

3.4. Within-canopy profiles

Within-canopy gradients are difficult to quantitatively interpret, but help to identify source and sink areas. Figures 1 and 2 present concentrations of NH_3, NH_4^+ and AN plotted against height above the ground. Two solid lines, one the regression line fitted to the AN and $(NH_3 + NH_4^+)$ concentrations measured more than 2 cm above d, and the second indicating the location of the canopy top, are also plotted in each figure.
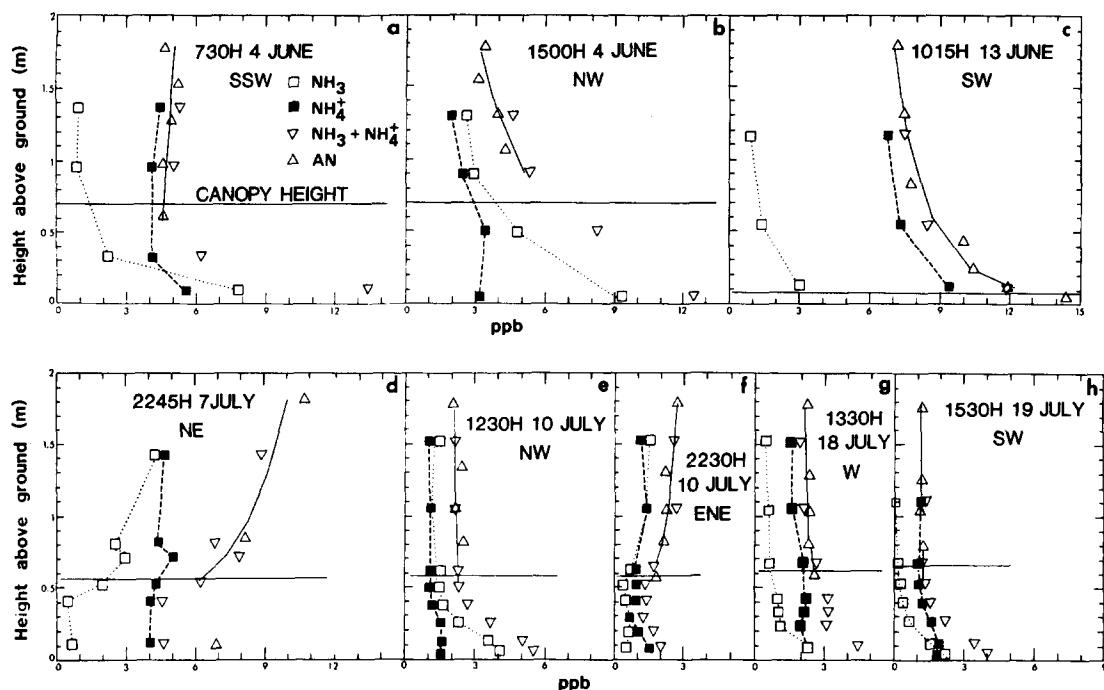
Fig. 1. Mean concentration profiles of NH_3, NH_4^+, $NH_3 + NH_4^+$, and AN measured during several runs (abscissa) vs height above the ground (ordinate). In each figure a regression line fitted between $\ln(z-d)$ and $(NH_3 + NH_4^+)$ and AN measurements made more than 2 cm above d is plotted as a solid line. The time that each run was started, the prevailing wind direction, and the height of the canopy top are indicated.
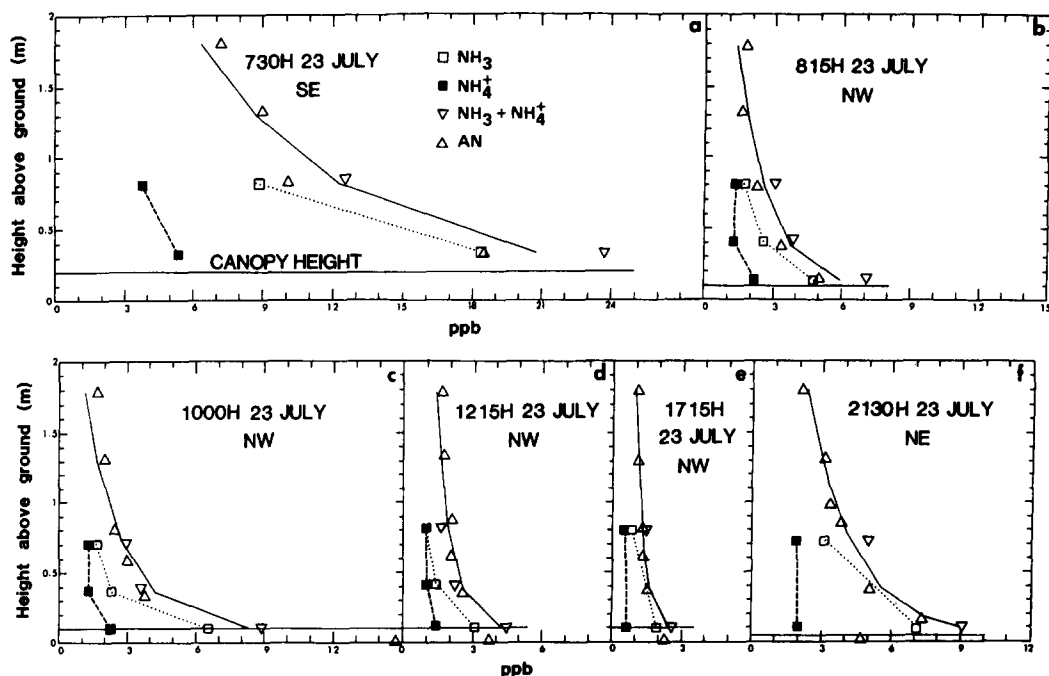

Fig. 2. Mean concentration profiles of NH_3, NH_4^+, $NH_3 + NH_4^+$, and AN measured during several runs made during the hay cutting period on 23 July. The portion of the field to the east of the sampling mast (upwind in Figs 2a and f) had been rain damaged; the western half of the field (Figs. 2b, c, d and e) had hay curing in good condition.

Daytime profiles frequently had elevated NH_3 concentrations close to the ground surface, decreasing monotonically with height to low values near or above the top of the alfalfa canopy. Prior to its first cutting, the alfalfa was in the first-bloom growth stage and had a heavy and dense canopy to a height of approximately 0.7 m. Many of the lower alfalfa leaves were heavily shaded. A total of 75 mm of rain had fallen during the two days preceding the runs represented in Figs 1a and 1b, so the soil surface was moist. Relatively high concentrations of 8–9 ppb of NH_3 were measured in the lower portions of the canopy, and NH_3 appeared to be leaking from or through the canopy to the atmosphere. In contrast, prior to second cutting, although canopy heights were similar, the canopy was less dense, and NH_3 concentrations in the lower canopy were only 2–4 ppb (Figs 1e, 1g and 1h). The soil surface was quite dry during these runs. The alfalfa was in the early bloom stage on 10 July and at full bloom on 18 July. Considerable leaf-miner damage to alfalfa leaflets was noted between 7 and 12 July; however, filter papers treated with cobalt chloride (Molga, 1962) indicated the alfalfa was transpiring freely during this period. The same technique indicated the alfalfa was somewhat stressed on the afternoons of 14 and 18 July.

During many night-time runs, profiles exhibited a minimum in the upper canopy (Figs 1d and 1f). During these runs, the leaflets of the alfalfa were usually folded closed and dew and/or guttation were present. Strong temperature gradients through the canopy occasionally interfered with sampling because condensation occurred within the glass tube traps and condensate may have been carried into the filter paper traps. For this reason, it is probable that NH_3 was underestimated and the NH_4^+ overestimated at the lowest sampling height in Figs 1d and 1f.

Figure 2 illustrates a series of profiles made over curing alfalfa hay. The sampling mast was located between two halves of the field, which had been cut at different times. Figure 2a represents the profile on 23 July above hay that had been cut 19 July and had been ruined while in wind rows by rain on 20 July. High concentrations of NH_3 were measured at 30 cm above the soil surface, and NH_3 could be smelled if one picked up a spoiled windrow, indicating local concentrations in excess of 7000 ppb (National Research Council, 1979). About 800 h EDT the surface wind shifted to the NW, and profile measurements were made over an area of the field that was cut on 22 July and had not been rained on. Because of the recent rain, the soil surface was moist. Close to the ground, maximum NH_3 concentrations were observed early in the day and declined during the afternoon as the hay and soil dried. In the evening, the wind again shifted and measurements were made over the spoiled area. During the day the hay from this area had been baled and removed. Nevertheless, elevated surface NH_3 concentrations, the source of which was probably shattered debris, were again evident.

As previously noted, the particulate fraction frequently dominated the total AN measurement during clear-hazy days when the winds were from the W or SW. An example of this difference was evidenced on 4 June. A frontal passage during the day resulted in the replacement of a warm, hazy SW flow (Fig. 1a) by one considerably clearer and drier (Fig. 1b). During several periods when hazy conditions prevailed, NH_3 was reduced to levels less than 1 ppb within 2 m of the ground (Figs 1a, 1c, 1g and 1h). This decline in NH_3 could be due to turbulent mixing, but it may also result from NH_3-to-NH_4^+ conversion within the lowest meters of the atmosphere.

3.5. Gas-to-particle conversion

The adsorption of NH_3 by acid aerosols could affect the observed gradients of both species. If, for the sake of argument, a surface NH_3 source and a small surface sink of NH_4^+ are assumed, rapid absorption of NH_3 by acid aerosols could decrease near-ground NH_3 concentration, thus decreasing the steepness of the above-canopy NH_3 gradient, and could concurrently reduce or even change the sign of the NH_4^+ gradient. Uncertainty concerning the absorption capacity of acid aerosols, the concentration of acid gases, the relative rates of the reaction and turbulent mixing, and of aerosol dry deposition to vegetated surfaces make it impossible for a simple analysis to distinguish between an NH_4^+ gradient created by a surface particulate source or by gas-to-particle conversion.

If acid aerosols rapidly react with NH_3 evolved from soil and plant surfaces then measurement of fluxes of both species is complicated because neither NH_3 nor NH_4^+ are conserved species in the lowest meter of the atmosphere. Common micrometeorological methods employed to estimate surface fluxes are appropriate only to conserved species (Fitzjarrald and Lenschow, 1983; Duyzer et al., 1983). Harrison et al. (1989) considered the possibility of gas-to-particle conversion resulting from reactions of NH_3 with HNO_3 and concluded the reaction was too slow to affect profiles close to the ground. However, the rate of reaction of NH_3 with acid sulfate aerosols may be faster (Charlson et al., 1974).

The rate of steady state heterogeneous condensation of a gas on a spherical particle in an infinite medium may be expressed (Friedlander, 1977, his equation 9.11):

$$F = 2\pi d_p D(p_1 - p_d)/kT \qquad (8)$$

where F is the number of molecules per unit time, d_p is the particle diameter, D is the molecular diffusivity of the condensing species, p_1 is the partial pressure of the condensing species in the medium, p_d is the partial pressure at the particle surface, k is the Boltzmann constant, and T the absolute temperature. In order to estimate the possible magnitude of gas-to-particle conversion, (8) was employed assuming a particle density of $1.5\ \mu g\, m^{-3}$, a particle diameter of 1 μm, a partial pressure difference of 1 ppb between the free

air and the particulate surface, and an atmospheric burden of reactive particulates of $15\,\mu g\,m^{-3}$. The resulting rate of heterogeneous condensation was $0.002\,\mu g\text{-N}\,m^{-3}\,s^{-1}$ or $0.07\,g\text{-N}\,ha^{-1}\,h^{-1}$ within the first meter of the atmosphere. The result varies inversely with the square of assumed particle diameter so that using a diameter of $0.2\,\mu m$ would increase the calculated condensation rate twenty-five-fold. Equation (8) applies only if gas-phase diffusion limits the reaction rate and each collision of a gas molecule with a particle results in reaction. Cadle and Robbins (1960) found that only one in 10 collisions of NH_3 with concentrated H_2SO_4 aerosols resulted in reaction while 100% of collisions were effective in dilute (12% H_2SO_4) droplets.

Transport within dense plant canopies is slower and relative humidity is usually higher than over bare soil. The above calculations illustrate that, in the presence of incompletely-neutralized acid aerosols, within-canopy gas-to-particle conversion could account for the observed above-canopy NH_4^+ gradients. However, since release of particles by vegetation has been reported (Beauford et al., 1977), the surface NH_4^+ source strength remains a question.

3.6. The NH_3 compensation point

In principle, if physiological resistances within the plant are negligible, the ammonia compensation point, NH_{3C}, may be inferred from measured concentrations (C_N) and gradients of NH_3 by using (5) and (9).

$$NH_{3C} = C_N - r_T(u_* N_*). \qquad (9)$$

However, if gas-particle reactions occurred predominantly below the gradient measurement heights (e.g. within the canopy), then gradients (and to a lesser extent concentrations) of NH_3 would be reduced and extrapolation using NH_3 gradients would yield underestimates of the true NH_{3C}. Better estimates would be obtained from extrapolation using gradients of AN, a conserved species, since then NH_{3C} would be underestimated only as much as NH_3 at the reference elevation was reduced.

Calculations of NH_{3C} were made using measured r_a and r_b; r_c estimates of 0, 25 and $50\,s\,m^{-1}$; ambient NH_3 concentrations; and gradients of either NH_3 or AN. Only data for daytime (run starting more than $1.5\,h$ after sunrise or more than $1.5\,h$ before sunset) periods when canopy vegetation was dry were used. Data from runs with NE winds and for periods within 10 days after hay cutting were also excluded.

Compensation point estimates based on extrapolation using NH_{3*} averaged between 2 and 3 ppb, while estimates based on AN_* were between 5 and 6 ppb (Table 4). The 2–3 ppb estimate implied by NH_{3*} is lower than the range reported for other species by Farquhar et al. (1980) and is lower than the value suggested by the work of Meyer (1973). The 5–6 ppb estimate is consistent with both the previous studies. This consistency with previous estimates suggests that

Table 4. Ammonia compensation point* during dry daytime conditions inferred from gradients of $NH_3(NH_{3*})$ and of $AN(AN_*)$

Resistance formulation	Number of observations	From NH_{3*} (ppb)	From AN_* (ppb)
$r_a + r_b + 50$	25	2.3 ± 1.0	6.2 ± 1.7
$r_a + r_b + 25$	25	2.1 ± 0.7	5.0 ± 1.2
$r_a + r_b$	25	1.9 ± 0.5	3.7 ± 0.8

* Mean $\pm$ standard error of mean. Mean NH_3 concentration at a reference elevation of 1 m above d was 1.4 ± 0.2 during these runs.

gas-to-particle conversion is significant. This conclusion must be regarded with caution, however, since all previous compensation point measurements were made under growth chamber conditions. It is therefore concluded that either gas-to-particle conversion takes place close to the ground and within plant canopies, or that the compensation point of field-grown alfalfa for NH_3 is lower than previously reported and a near-ground source of NH_4^+ exists, or both.

Further caution is needed. If NH_3 originating from the soil or from decaying debris (Whitehead and Lockyer, 1989) were leaking through the canopy, or if compensation points were higher for shaded (and possibly senescing) leaves in the lower canopy, then the compensation point of young top leaves could be lower than those reported in Table 4. As previously noted, some within-canopy profile shapes (Figs 1 and 2) indicated a ground or lower-canopy source of ammonia.

4. CONCLUSIONS

Our results are consistent with previous observations in that concentrations of NH_4^+ generally exceeded those of NH_3 at heights of 1–2 m above the land surface, however the NH_3 concentration frequently exceeded that of NH_4^+ closer to soil/plant surfaces. At 1 m above the crop's displacement plane, NH_3 averaged 1.7 ppb except when the wind was from the NE when flows averaged 4.8 ppb reflecting the presence of local sources. Ammonium concentrations varied consistently with synoptic wind direction with concentrations being lowest for NW flows, 2.2 ppb, and highest for SW flows, 6.9 ppb. Concentrations and gradients of both species were higher during and following periods of hay harvest when the alfalfa field acted as an ammonia source during both day and night.

Within-canopy NH_3 gradients were much steeper than those of NH_4^+, while above-canopy gradients of NH_3 and NH_4^+ accounted for 63% and 36%, respectively, of independently measured AN gradients. It is possible that NH_4^+ gradients resulted from gas-to-particle conversion within the lowest meter of the

atmosphere rather than from a true surface NH_4^+ source. Apparent leaf surface NH_3 concentrations close to zero were estimated during periods when vegetation was wet with dew or guttation. Gaseous gradients indicated an NH_3 compensation point of 2 ppb under dry daytime conditions, lower than previously published estimates. However, conversion of NH_3 to NH_4^+ within the canopy air could have resulted in an underestimation of the compensation point.

The NH_4^+ fraction is probably less surface reactive than NH_3, but acid aerosols may play a significant role in ammonia exchange. By absorbing NH_3 and maintaining a low gas concentration in canopy air, aerosols may compete with plants for NH_3. Since high AN is frequently associated with low NH_3, total AN is a poor predictor of soil–plant–atmosphere ammonia exchange. Future studies of ammonia exchange with vegetation or land surfaces should consider the relative contributions of NH_3 and NH_4^+ to AN concentrations and gradients if flux densities are to be related to ambient conditions.

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